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MASS SPECTROMETRIC STUDIES OF MOBILITIES, DIFFUSION, AND REACTIONS OF IONS IN GASES

By

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FINAL REPORT

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ABSTRACT

A long term research program has been continued, utilizing a Drift Tube Mass Spectrometer apparatus for basic studies of the drift velocities and mobilities, the diffusion coefficients, and the rates of reactions of low-energy ions in gases. Encouraging progress has been made in the current period toward the extension of the data analysis capability to include situations where a pair of ion species are coupled by a reversible reaction having arbitrary rates in either direction. In pure carbon monoxide, the primary ion CO^+ and the secondary dimer ion $CO \cdot CO^+$ constitute a typical such pair of species. A very detailed experimental study of this case has been underway to evaluate and confirm the extended analysis.

I. INTRODUCTION

This report deals with the progress in the Georgia Tech drift tube research program during the period in which the work was partially supported by the U. S. Air Force Office of Scientific Research under Grant No. AFOSR 70-1933. The period involved was from July 1, 1970 through June 30, 1971.

The research performed during this period has been a continuation of a program which has been in progress at this institution for a number of years, and has received continuous support from AFOSR since its inception. A rather comprehensive report on the entire program up to that time was issued in July, 1970 (AFOSR Accession No. 70-1994TR), at the termination of the immediately preceding Grant, No. AF-AFOSR 1118-66. The present report will be limited mainly to discussion of the specific progress of the current period.

II. OBJECTIVES AND METHODS

This research involves the use of an apparatus which we call a drift tube mass spectrometer, which was developed by the present authors earlier in this program, for study of the mobilities, diffusion coefficients, and reactions of low-energy ions in gases. In this apparatus, very brief and low-density bursts of ions are injected into the gas, by a pulsed ion source at one end of a large drift space. As the swarm of

ions drifts in a weak electric field maintained across this space, the ions diffuse both longitudinally and transversally with respect to the field direction, and may undergo reactions with the molecules of the gas to form new ions of various molecular compositions. At the far side of the drift space, some of the arriving ions pass out through a sampling orifice, and through a mass selector to a detector which responds to the arrival of a single ion. The detector signals are electronically sorted according to the time elapsed since the source pulse. The accumulation of counts from a large number of such bursts provides a time profile of the drifting swarm of ions of a known molecular composition at a known distance from the ion source. A number of such profiles, for every ion species found to be present in the gas, and for various values of the drift distance, gas pressure, electric field strength, and other parameters of the experiment, constitute the raw data from which the quantities of interest are to be determined. An important feature of the present apparatus, which continues to be unique among others of this type, is that the ion source is movable, so that the drift distance may be varied. This feature makes possible the extraction of much more information from the data than would otherwise be the case.

The analysis of the data involves the fitting to sets of experimental time profiles of analytical profiles computed from a mathematical model of the experiment. Great care has been taken to assure that the idealized geometry of the model is approximated closely in the real experiment. The quantities of interest occur as parameters in the analytical computations, and are in principle determined by adjusting their values for the best fit. This fitting is by no means an automatic procedure that

can be simply left to a computer, however, because of the number of parameters involved. It has been demonstrated that in favorable cases, several of the parameters can be quite accurately determined almost independently of the others, by various special methods of selecting and processing the data. A continuing thrust of this program has always been aimed at the further development and detailed testing of such special methods. The goals of this effort are to obtain more accurate and reliable values for the quantities of interest, to extend the evaluations to wider ranges of the experimental conditions and/or to a wider variety of cases, and especially to obtain values for quantities that have never before been accessable to measurement.

The lengthy report of one year ago, already mentioned, contains a general description of all of the special methods which had been developed and investigated up to that time. This information will not be repeated here, but there follows a brief summary of the types of actual measurements which had been accomplished through the use of these methods. In this discussion the parameter E/N, the ratio of the applied electric field strength to the gas number density, is the quantity which determines the mean energy or"temperature" of the ions in the swarm. The term "low E/N" means values small enough (less than about 10 Td, or "Townsends", where 1 Td = 10^{-17} Volt cm^2) that the ions remain essentially in thermal equilibrium with the gas; the term "high E/N" implies values large enough (more than 30 to 50 Td, depending on the case) that the mean ion energies become appreciably greater than the thermal energy.

For primary ions (those initially formed in the ion source), the drift velocity and mobility could be determined quite easily with

uncertainties of only about 2 or 3% under nearly all circumstances. The only exception encountered had been the case of an ion (H_2^+ in H_2 gas) that was so rapidly depleted in a 2-body reaction that it scarcely had a well-defined mobility at all. In all other cases encountered, the determination could be extended to low E/N, at which the mobility had become constant at its "zero-field" value. The longitudinal (along the field direction) diffusion coefficient D_L had also been determined for most cases over a range of E/N, with uncertainties as small as about 10% at low E/N. Our determinations of D_L have been the first known direct determinations of this quantity ever published for ions in gases. Our results have shown generally good agreement with a theoretically predicted relation to the mobility at low E/N (the Einstein Relation), but increase very rapidly to several times this value at higher E/N. The transverse diffusion coefficient D_T had been separately and independently measured, in a lesser number of cases in which the pattern of reactions of the ions with the gas was sufficiently simple, and in which the rate coefficients were not too large. Our results have shown a definite distinction between D_L and D_T as both increase from the Einstein value with increasing E/N, and have been the first known observations of this effect for ions. The identification, order, and rate coefficients of reactions which deplete a primary ion swarm during its drift had also been determined in several favorable cases, with uncertainties in the rate coefficient of as little as 10%. With only a few exception, other measurments of these same rate coefficients have had a much lower accuracy, and often were little better than order-of-magnitude.

For secondary or daughter ion species, formed in reactions between the primary ions and the gas, only slightly less accurate determinations of the drift velocity and mobility had been possible in some cases, where the pattern of reactions was not too complex and the ratios of some of the rate coefficients were favorable. Both reliable "zero-field" mobilities and the trend toward higher E/N had been obtained in these cases. However, no serious attempts at the evaluation of diffusion coefficients for secondary ions had as yet been undertaken in this earlier period.

A situation of real practical interest, which is not at all uncommon, is that in which secondary ions may undergo a "reverse" reaction that re-creates "tertiary" ions of the same molecular species as the true primary ions. Our previously proven methods have been unable to deal with this situation in general, although the forward reaction rate could sometimes be obtained if the rate of the reverse reaction was small enough, and if the mobilities of parent and daughter species were markedly different. However, a special method for the case that both reactions have rates so large that the parent and daughter species coexist in the swarm in a sort of secular equilibrium had also been investigated briefly. This method is limited to special cases where the two ion species have nearly identical mobilities and diffusion coefficients, and had yielded only rather qualitative results for the single case to which it was applied.

Studies in 5 different gases of atmospheric interest, of all primary ions formed from the parent gas by electron bombardment, and of all secondary ions formed from the primaries by reactions with the gas, had been

carried out in the previous periods of this program. A summary listing of these cases and of the results obtained for each is contained in the previous report, and will not be repeated here.

III. PROGRESS DURING THE CURRENT PERIOD

A. Analytical Developments

The previously developed analytical model of the experiment included a general treatment of the forward-backward reaction situation already mentioned, but the usefullness of these results in the analysis of real data had not as yet been investigated. The principle developments of the current period have been in this area. The analytical expressions are of a sufficiently complex form that it is by no means immediately evident just how sensitive the shapes of the predicted profiles will be to the assumed values of each of the many parameters involved, i.e., the mobilities and diffusion coefficients of the parent and daughter ion species, the rate coefficients of the forward and backward reactions and of any other reactions that may be present, and of the relative amount of the daughter species that may be created in the ion source before the burst is gated into the drift tube. A determination of the actual usefullness of the results requires an extensive and systematic study of these matters, including many comparisons with an extensive body of suitable experimental data.

Computer programs have been perfected which calculate detailed theoretical profiles for both the parent and daughter species for any given choice of the values of all of the parameters. Many such profiles have been calculated and compared with one another. A number of interesting

generalizations have emerged from these studies, in the form of statements about a particular feature of the profile shape that is most sensitive to the value chosen for a particular one of the parameters. Additional comparisons with real experimental data have been initiated, and are still in progress at the time of this writing.

The results obtained thus far appear to be very encouraging. Although certain difficulties have appeared, the indications are that this multi-parameter fitting procedure will actually be able to yield reasonably firm values for most of the quantities of interest in the reversible reaction case, over a range of conditions that will represent a substantial increase in our capabilities. These conclusions remain somewhat preliminary at the present time, however, and therefore a more detailed description will not be undertaken in this report.

B. Experimental Studies

Following the conclusion of the study of nitric oxide, which was largely covered in the last report, we turned to the study of carbon monoxide, which has occupied the bulk of the present period. The only ion species of significant abundance observed in the very pure gas are the primary ion CO^+ and the secondary "dimer" ion $CO \cdot CO^+$. The dimer ion is only loosely bound, and can be observed to dissociate back to CO^+ and CO at higher E/N. Thus we have here a simple system of only 2 ion species of quite different mobilities, involved in a reversible reaction scheme of the type discussed above, with no significant competing reactions or other complications. Hence this appears to be an ideal case for the experimental study of the forward-backward analysis.

It has been in the pursuit of this interest that the carbon monoxide studies have been extended longer than initially planned, and in fact

they are not yet concluded at the present time. Following some initial difficulties with impurities, to be mentioned further below, data were obtained which yielded, by our previously developed methods, the mobilities of both species and the longitudinal diffusion coefficient of the primary ion. The study of the forward-backward analysis has, however, required a large amount of additional data. The detailed profiles needed for this study require relatively long counting times to attain adequate counting statistics far down the sides of the profile, with special attention given to stability during these long counts, and to several other factors.

If all of our expectations regarding the forward-backward analysis are actually realised, the final results of the carbon monoxide study will be far more comprehensive than those of any of our previous studies. Pending the final results, none of the simpler results of the early part of the study have as yet been prepared for publication, and they will not be presented here.

Journal articles presenting the results of the nitric oxide study, and of the previously completed studies of oxygen, were completed during the current period and have been published. The references are given in the publications section of this report.

C. Modifications of Apparatus and Procedures

In the early part of the present period it became necessary to carry out an extensive disassembly of the apparatus, the first in several years, in order to deal with an accumulation of minor problems. The opportunity was taken to make several changes at that time which had been pending.

The ion sampling orifice at the exit end of the drift tube was changed back to its original size. A smaller orifice had been installed during the earlier oxygen studies, to accommodate the higher drift tube gas pressures

required for parts of that study. When such higher pressures are not required, the smaller orifice imposes an unnecessary restriction on the sampled ion intensity. It had not been removed sooner simply because the construction of the apparatus is such that this is a major operation requiring extensive disassembly.

A new rf quadrupole mass selector of improved capabilities which had recently been procured was also installed at this time. Our reasons for replacing the previous selector were given in the last report. The new instrument has proved to be very satisfactory, and has lived up to all expectations.

The type of electron emitting filament used in the ion source was also changed at this time. Although this operation can be performed without such extensive disassembly, it normally entails an interruption of the experimental work for at least several days. The thoriated iridium filaments used in our earliest studies had proved to be prohibitively short-lived in oxygen at the higher pressures involved in that study, requiring a change at that time to an oxide coated filament of platinum gauze. The latter filament had remained in use ever since, despite the serious disadvantage that it required much more heating power for a given emission, which heats the apparatus locally, causes temperature gradients, and therefore interferes with the determination of any rate coefficient with a strong temperature dependence.

We know of no reliable general guide to the expected performance of different types of filaments in the varied gases and at the pressures involved in our experiments. To avoid having to experiment with filaments in the main apparatus, a small auxiliary apparatus with a simple vacuum system was

assembled, in which filament life tests are to be conducted in advance in each gas slated for study. Since such tests indicated satisfactory performance of the thoriated iridium filament in carbon monoxide, a filament of this type was again installed.

It was mentioned in the preceding section that the early measurements in carbon monoxide were hampered by impurities. Specifically, the problem was with water vapor in the feed gas; the same problem had also caused considerable trouble in the earlier nitric oxide studies. One of the most effective ways to remove water vapor from the feed gas is to pass it through a trap maintained at the lowest possible temperature. We have previously relied on a simple coil trap immersed in a liquid refrigerant. Because NO and CO would themselves condense at the atmospheric boiling point of liquid nitrogen, these gases had been trapped only at the much higher temperature of a dry ice and acetone mixture.

A new trap has been constructed having a coil suspended in the cold vapor above a liquid nitrogen surface, inside a closed steel Dewar flask which can be pressurized if desired. A heating wire on the coil itself can be used to increase its temperature, while power applied to a second coil immersed in the liquid nitrogen can increase the vapor streaming rate to lower the temperature of the suspended trap. An automatic circuit switches the power to these coils as required, in response to the readings of a thermocouple affixed to the lowest part of the trap coil. This device can maintain the trap continuously just a few degrees above the condensation temperature of CO, and has effectively solved the water vapor problem in this gas.

A final development of the current period involves our method of gas pressure calibration. Our "on line" pressure sensor is a Baratron capacitance manometer, which is sensitive and linear in our usual pressure range, but is not absolute, and is subject to possible long-term drifts. This instrument was initially calibrated against a McLeod gauge, with a minimal possible error of at least 2%, which was attributable mostly to the well known vagaries of the McLeod gauge itself. We have long sought a means for periodic recalibration of our Baratron which would be more convenient and more reproducible than the McLeod gauge.

It has been noted that several relatively recent measurements of the zero-field mobility of potassium ions in nitrogen agree within 0.5% with one another, and with our own measurement of about 3 years ago, within its assigned error. Several of these independent measurements were made at much higher gas pressures than ours, which could be measured with a smaller probable error. We consider that this number is now well established to be 2.54 ± 0.01 $cm^2/Volt\ sec$, and have adopted this value as a secondary standard on which to base our own pressure calibration.

Early in the present period we remeasured this quantity, using our existing calibration of the Baratron. Our results were readily repeatable within 1%, and agreed within about 1% with the above value, and with our own earlier value. Accordingly, we now presume that the initial calibration of our Baratron was actually correct to within 1%, and has remained stable within about 1% over a period of more than two years. In the publication of the results of our studies of both oxygen and nitric oxide, we therefore reduced our estimate of the probable error in the gas pressure measurement from 2% to 1%. Correspondingly, the estimate of the possible systematic

error in our mobility values was reduced from 4% to 3%.

We have modified the gas feed line of our apparatus to provide for the permanent connection of a cylinder of nitrogen, so that regular checks of our Baratron calibration can be carried out frequently and conveniently. A short paper recommending the general adoption of this calibration procedure has been published in The Review of Scientific Instruments.

IV. APPLICATIONS

During the present period, Dr. E. W. McDaniel has been serving as a consultant to the Franklin GNO Corporation. This firm is developing a line of instruments for the detection, identification, and measurement of minute-level impurities in air. The principles of these instruments involve many of the techniques and some of the results of the present research program, as well as those of related programs elsewhere.

The common feature of these instruments is an atmospheric-pressure drift tube into which the air to be analyzed is drawn. A radiation source provides a supply of primary ions of the atmosphere itself, i.e., chiefly of nitrogen. As these ions then drift in the direction of a low E/N applied field, almost any sort of organic impurities present will be selectively and efficiently ionized through charge transfer collisions with the primary ions, because of the relatively high ionization potentials of the atmospheric primary ions. As we have frequently noted in discussing the problems that impurities create in our experiments, it is quite possible for the ions in the stream, at a point "downstream" from the source, to consist predominantly of impurity-species ions, even if the neutral impurity is present in the air in only very low relative abundance. Thus the selective ionization of the impurities by charge transfer during low E/N drift is utilized to

enhance the current of impurity ions, relative to the current of primary atmospheric ions, by a large factor.

In the simpler of 2 basic versions of this device, the current of impurity ions is distinguished from the current of any remaining primary ions on the basis of a mobility measurement; short pulses of the ion stream are gated periodically into a further section of the drift tube, and are detected as a function of time at a point still further downstream. The molecular weights of many organic impurities of great interest are large compared to those of the atmospheric gases, and the mobilities should be correspondingly lower. The resulting time separation of the impurity and primary ion pulses serves not only to distinguish them from each other, but also further enhances the sensitivity for detecting impurity ions in the presence of much larger numbers of atmospheric ions. Furthermore, it may sometimes be possible to distinguish certain impurities from one another on the basis of their mobilities, if the number of possible impurities involved is not too large.

In a second and more elaborate version of this device, the instrument is basically a drift tube mass spectrometer, which can provide a much more positive identification of the impurity species than is possible from mobility measurements alone.

The indications are that these devices can prove useful in the detection and identification of impurities present to only one part in 10^{10} to 10^{11} of air. There is obviously a fascinating array of potential technological applications for such a powerful device in commercial, environmental, and scientific areas. A few such possibilities include the detection of pesticide contamination of foods, water, and air, the medical diagnostic analysis of exhaled breath, or of the vapor of urine or blood samples, commercial

applications in the perfume industry, and probably any number of military applications. It is understood that one of the Franklin GNO instruments is already finding application in a basic, scientific study of the formation of ions in the lower atmosphere, conducted by Dr. V. Mohnen of the Atmospheric Sciences department of the State University of New York, in Albany, N. Y.

V. PUBLICATIONS AND REPORTS

A. Articles

1. "Review of 'Electronic and Ionic Impact Phenomena,' Vols. I and II, by Massey and Burhop," by E. W. McDaniel, Am. J. Phys. 38, 551 (1970).

2. "Reply to 'Longitudinal Diffusion Coefficients Misnamed,' by R. N. Varney," by I. R. Gatland and E. W. McDaniel, Phys. Rev. Ltrs. 25, 1603 (1970).

3. "Mobilities and Longitudinal Diffusion Coefficients of Mass-Identified Potassium Ions and Positive and Negative Oxygen Ions in Oxygen," by R. M. Snuggs, D. J. Volz, J. H. Schummers, D. W. Martin, and E. W. McDaniel, Phys. Rev. A 3, 477 (1971).

4. "Ion-Molecule Reactions Between O^- and O_2 at Thermal Energies and Above," by R. M. Snuggs, D. J. Volz, I. R. Gatland, J. H. Schummers, D. W. Martin, and E. W. McDaniel, Phys. Rev. A 3, 487 (1971).

5. "Review of 'Introduction to the Theory of Ion-Atom Collisions,' by M. R. C. McDowell and J. P. Coleman," by E. W. McDaniel, Am. J. Phys. 39, 237 (1971).

6. "Suggested Use of the Known Mobility of K^+ Ions in Nitrogen Gas for Pressure Calibration in Atomic Collisions Experiments," by E. W. McDaniel and D. W. Martin, Rev. Sci. Instr. 42, 157 (1971).

7. "Tests of the Wannier Expressions for Diffusion Coefficients of Gaseous Ions in Strong Electric Fields," by E. W. McDaniel and J. T. Moseley, Phys. Rev. A 3, 1040 (1971).

8. "Mobilities and Longitudinal Diffusion Coefficients of Mass-Identified Potassium and Nitric Oxide Ions in Nitric Oxide," by D. J. Volz, J. H. Schummers, R. D. Laser, D. W. Martin, and E. W. McDaniel, Phys. Rev. (in press, 1971).

B. Books

1. "Case Studies in Atomic Collision Physics," Vol. II (edited by E. W. McDaniel and M. R. C. McDowell), North-Holland Pub. Co., Amsterdam, in press.

2. "The Mobility and Diffusion of Ions in Gases," by E. W. McDaniel and E. A. Mason (a monograph in preparation).

C. Seminar Talks

E. W. McDaniel has presented seminar talks dealing with this research at the following institutions, during the period covered by this report.

Redstone Arsenal
Rice University
NASA Langley Research Center
Aberdeen Proving Ground
Texas A. and M. University
State Univ. of New York at Albany
Joint Institute for Laboratory Astrophysics, Univ. of Colorado

VI. PERSONNEL

A. Faculty Members

Drs. Earl W. McDaniel and David W. Martin, both Professors in the School of Physics of the Georgia Institute of Technology, have continued their longstanding collaboration in this research during the present period. Both have received direct financial support for their participation from this grant.

B. Postdoctoral Fellows

Dr. Donald J. Volz participated in this research during the early months of the present period. At the conclusion of his appointment in September, 1970, he assumed a faculty appointment at Voorhees College in Denmark, So. Carolina.

Dr. George M. Thomson has participated in this research since September, 1970.

Both Fellows have utilized equipment, supplies, and services supported by this grant, but neither has received direct salary support from the grant.

C. Graduate Students

John H. Schummers has participated in this research throughout the present period. He has been admitted to Candidacy for the Ph.D., and is currently engaged in his thesis program within the present research program.

Richard D. Laser participated in this research during a portion of the present period, but has recently terminated his enrollment after completing the requirements for the Master's Degree.

David R. James has participated in this research since September, 1970.

VII. RECOGNITION AND AWARDS

Dr. Earl W. McDaniel has been designated as the Georgia Scientist of the Year for 1971 by The Georgia State Science and Technology Commission.

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13. ABSTRACT

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Mobility						
Diffusion Coefficient						
Longitudinal and Transverse Diffusion						
Ion-Molecule Reaction Rate						
Reversible Reaction						
Dimer Ion						